

CHARACTERIZATION OF AMPHIPHILIC AND MICROPHASE SEPARATED GRAFT COPOLYMERS II SURFACE CHARACTERIZATION AND IN VITRO BLOOD-COMPATIBILITY ASSESSMENT OF POLYSTYRENE-GRAFT- ω -STEARYL-POLY(ETHYLENE OXIDE)*

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ABSTRACT

This paper reported the research results concerning the surface characterization of polystyrene-graft- ω -stearyl poly(ethylene oxide) (PS-g-SPEO) by means of XPS, contact angle measurement and TEM, and its in vitro blood compatibility assessment by measuring the plasma recalcification time (RT) and partial thromboplastin time (PTT). The XPS results demonstrated that the surface and bulk composition of the PS-g-SPEO graft copolymers differ remarkably from each other, and that SPEO component was constantly enriched at the copolymer/air interface. Contact angle studies indicated that the surface water wettability can be adjusted effectively by changing the composition of the copolymer. PS-g-SPEO graft copolymers can undergo microphase separation as clearly illustrated by TEM photographs. The relationship between the surface properties of PS-g-SPEO graft copolymer and its blood compatibility was also discussed.

INTRODUCTION

The research efforts in characterizing the surface properties of blood-

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compatible materials as related to their blood-contacting performances have been carried out^[1-7]. The accumulative results have demonstrated that it is very important and necessary to characterize the surface composition and structure of biomedical materials, since it is the surface features of these materials that direct their biocompatibility, and it has been widely accepted that blood compatibility, which is determined by the interaction of blood components, such as proteins, cells, etc., with a material surface, is influenced greatly by the surface characteristics.

A variety of polymers have been studied as biomaterials, among which PEO-based biomaterials, especially with long PEO side chains^[6,7], have been recognized as good blood-compatible materials. However, as far as surface properties and their relationship with biocompatibility are concerned, only block copolymers, for example, PEO-PS-PEO triblock copolymers^[8-10], or PEO-based polyurethanes^[11-13], have been studied intensively, but little is known about the surface features of graft copolymers, although a lot of work have already been done in the characterization of surface chemistry and wettability of amphiphilic block copolymers, such as PS-PEO diblock and PEO-PS-PEO triblock copolymers^[14-15].

Polystyrene-graft-*w*-stearyl poly(ethylene oxide) (PS-*g*-SPEO) is a kind of amphiphilic graft copolymer with long PEO side chains. On the basis of the published results about the synthesis, purification and bulk characterization of PS-*g*-SPEO^[16], this paper will report the surface characterization and in vitro blood compatibility assessment of PS-*g*-SPEO. The relationship between the surface properties of PS-*g*-SPEO and its blood compatibility will also be discussed.

EXPERIMENTAL

1. *Materials*;

A series of PS-*g*-SPEO samples with different SPEO contents but fixed number-average molecular weight ($\bar{M}_n$) of SPEO were prepared according to our published method^[16]. The ($\bar{M}_n$) of all the copolymer samples was around 20,000 and the ($\bar{M}_n$) of SPEO is fixed at 840.

2. *Surface characterization of PS- g -SPEO*

(1) Surface chemical composition of PS-*g*-SPEO by XPS

A. XPS sample preparation: The thin films of PS-*g*-SPEO for XPS

analysis were prepared by dip coating from dilute solution of PS-g-SPEO in chloroform (0.5% w/v) onto a flat aluminum substrate. The obtained films were dried overnight in vacuum at ambient temperature. Suitable thickness of the coatings were achieved by changing the solution concentration or by multiple dipping to insure the substrate Al_{2p} core level signal attenuated to an unobservable degree.

B. XPS instrumentation: Spectra were recorded on an ESCALAB MARK II spectrometer by using $Al_{K\alpha}$ exciting radiation. The basic pressure in the measurement chamber was kept around 1×10^{-8} torr. The value of 285.0 eV of the hydrocarbon C_{1s} core level was used as a calibration for the absolute energy scale.

Overlapping peaks were resolved into their individual components by means of the software dedicated in the XPS spectrometer. The detailed deconvolutions were based on a knowledge of binding energies and full widths at half maximum (FWHMs) from studies of corresponding homopolymers.

(2) Surface water wettability (amphiphilicity) of PS-g-SPEO by water contact angle measurement

The thin films for contact angle measurement were prepared by dip-coating from a 0.5% w/v solution of PS-g-SPEO in chloroform onto clean glass substrates and dried overnight at room temperature.

The contact angles, including static angles (θ_s), advancing angles (θ_a), and receding angles (θ_r), of distilled water on the surface of PS-g-SPEO films were measured by sessile drop method, employing a JY-82 apparatus. For each sample, ten to twelve separate drops were examined and the average contact angles were recorded.

(3) Microphase separated morphology of PS-g-SPEO by TEM

The samples of PS-g-SPEO graft copolymers were dissolved in chloroform at a concentration of about 0.5% w/v. Then the solution was coated directly on carbon-coated copper grids. After evaporation of the solvent, the thin copolymer films were exposed to the vapor of osmium tetroxide (2% w/v aqueous solution) at 40°C for 48 hours. According to the published results^[17], the PS chains on the PS-g-SPEO film surface were selectively stained. The morphology of the PS-g-SPEO film was observed by means of a transmission electron microscope (JEOL, JEM-100CX).

3. *In vitro* blood compatibility assessment of PS-g-SPEO

The interior surfaces of small glass tubes (12 × 75mm) were coated

with 1% w/v solution of PS-g-SPEO in chloroform. Then the recalcification time (RT) and partial thromboplastin time (PTT) of fresh human anticoagulant plasma on the coated surfaces were measured. For each sample, six separate RT and PTT values were examined, the average data were recorded and used as the parameter to comment the blood compatibility of PS-g-SPEO graft copolymers.

RESULTS AND DISCUSSION

1. The surface chemistry of PS- g -SPEO

(1) Homopolymer. In order to establish a firm basis for the interpretation of the graft copolymer data, it is necessary to study the component homopolymers, polystyrene (PS) and stearyl poly (ethylene oxide) (SPEO), and to determine their binding energies (E_b) and full widths at half maximum (FWHMs). The XPS core level spectra for PS and SPEO are shown in Fig. 1 and the experimental E_b and FWHM are tabulated in Table 1. The spectrum of PS has a strong peak centered at 285eV associated with the direct photoionization of the C_{1s} core level and a low-energy satellite peak at 291.6 eV arising from shake-up transitions ($\pi^* \leftarrow \pi$) accompanying core ionization (Fig. 1a). These low-energy shake-up transitions are understood both theoretically and experimentally and the spectrum observed in Fig. 1a is entirely consistent with the previous work^[18].

Table 1 The XPS binding energies and full widths at half maximum of PS, SPEO and PS-g-SPEO

Samples	Binding energies (eV)			
	C_{1s} peak shape	C_{1s}	$C_{1s}(\pi^* \leftarrow \pi)$	O_{1s}
PS	single	285.0(~ 1.8) ^a	291.6 (~ 2)	/
SPEO	overlapping	285.0(~ 1.8)+286.5(~ 2)		533.2 (~ 3)
PS-g-SPEO	overlapping	285.0(~ 1.8)+286.5(~ 2)	291.6 (~ 2)	533.2 (~ 3)

a: Data in the bracket are the values of FWHMs

The spectra of SPEO show a single peak for the O_{1s} core level at 533.2eV (Fig. 1d), and a doublet arising from the overlapping of a C_{1s} peak of stearyl at 285eV and a C_{1s} peak of PEO at 286.5eV. The binding energy for C_{1s} core of stearyl is the same as that for C_{1s} core of polystyrene. And as expected, there is no shake-up peak in the C_{1s} core level spectrum of SPEO

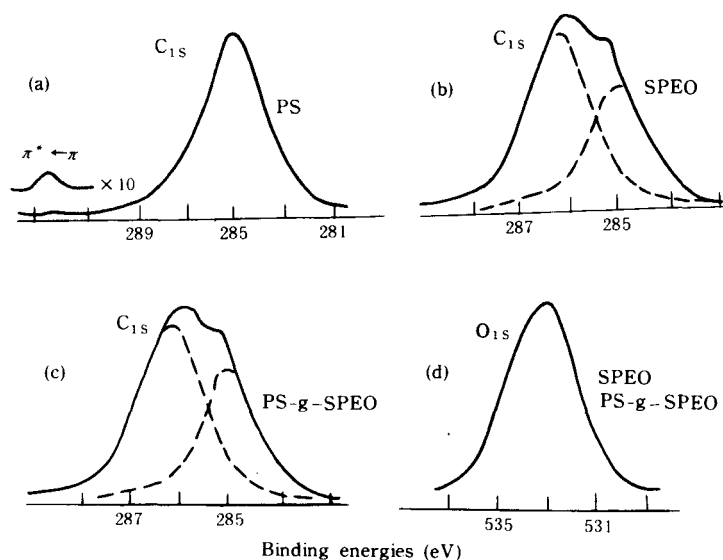


Fig. 1 C_{1s} core level XPS spectra for PS (a); SPEO (b); PS-g-SPEO (c) and O_{1s} spectrum for SPEO and PS-g-SPEO (d)

since stearyl and PEO are fully saturated. The chemical shift of 1.5 eV for the C_{1s} core level peak in PEO, relative to PS and stearyl, can be attributed to each carbon being attached to oxygen atom and is consistent with theoretical predictions and experimental results on related low molecular weight model compounds^[19]. This significant difference in the XPS spectra of stearyl and PEO, i. e., the 1.5 eV chemical shift in the C_{1s} core level, make it easy to deconvolute the doublet C_{1s} peak into two peaks which correspond to C_{1s} peak of stearyl and C_{1s} peak of PEO. The result indicates that the peak area ratio of C_{1s} peak for stearyl to that for PEO, i. e., $C_{1s}(\text{stearyl})/C_{1s}(\text{PEO})$, equals to 0.67, which means that the ratio of the surface carbon atom numbers of stearyl to that of PEO is 0.67.

As we know, an interface will always attempt to achieve the lowest interfacial energy. If a polymer system contains more than one component, the component that, when localized at the interface will result in a minimum interfacial energy, will, if possible, migrate to the surface. Thus, for a copolymer/air interface, the lowest energy component (or functional groups) in the polymer will accumulate at the interface. The critical surface tension for n-hexadecane, PS and PEO is 19.5, 33 and 43 dyne/cm^[20]. Therefore, it is expected that the stearyl will be enriched at SPEO/air

interface. However, the measured ratio of the surface carbon atom numbers for stearyl to that for PEO, 0.67, is very close to the calculated value of the ratio of the bulk carbon atom numbers of stearyl to that of PEO, 0.69, which is calculated from the formula of SPEO:



This result indicates that the surface composition and bulk composition of SPEO do not differ from each other, which means that stearyl is not enriched at SPEO/air interface.

The degree of molecular mobility of the polymer determines that whether energetically desirable minimization of interfacial energy can indeed be achieved. Both chains of stearyl and PEO are fairly short since SPEO has a relatively low molecular weight (840). Thus, the mutual restriction function between chain motion of stearyl and that of PEO is supposed to be rather strong, which means that PEO chains can be constrained to migrate towards SPEO/air interface simultaneously when stearyl groups migrate to the interface. And the flexibility and high mobility of PEO chains enable this "constraint effect" be carried out in a rather complete degree. As a result, stearyl group and PEO move as a whole and has almost the same probability of appearing at the interface.

(2) Graft copolymer: The spectra of PS-g-SPEO exhibit the characteristic peaks of both PS and SPEO, and have also two peaks: one single peak for the O_{1s} core level at 533.2 eV (Fig. 1d) and one overlapping peak for the C_{1s} core level (Fig. 1c). This overlapping peak was easily deconvoluted into two peaks: a C_{1s} peak at 285 eV for both PS and stearyl, and a C_{1s} peak at 286.5 eV for PEO. Accordingly the area ratio $\text{C}_{1s}(\text{PS} + \text{stearyl})/\text{C}_{1s}(\text{PEO})$ was obtained, and then the surface SPEO content can be derived from the value of $\text{C}_{1s}(\text{PS} + \text{stearyl})/\text{C}_{1s}(\text{PEO})$ and the molecular structure of PS-g-SPEO.

A: Effects of stearyl end group on the surface chemical composition of PS-g-SPEO.

As shown in Fig. 2, the surface and bulk composition of PS-g-SPEO differ remarkably from each other, and the SPEO component is constantly enriched at the PS-g-SPEO graft copolymer/air interface which differs from that of PS-g-PEO in which the PS component is enriched at the PS-g-PEO graft copolymer/air interface^[21]. These results indicate that the nature of the side groups (PEO or SPEO) will have great influence on the surface enrichment (accumulation) phenomenon.

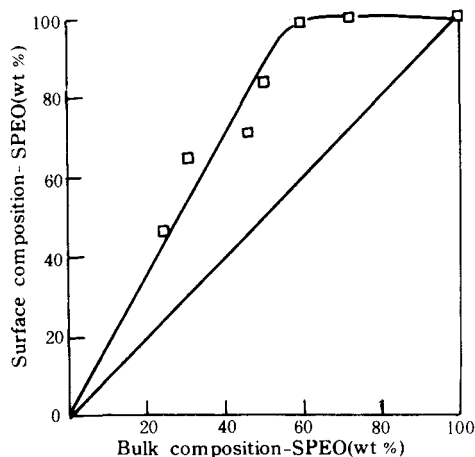
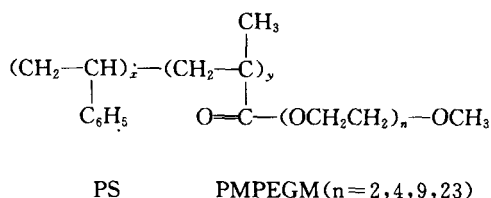


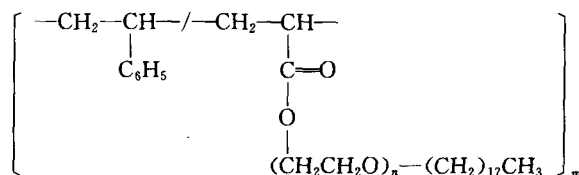
Fig. 2 Surface vs. bulk composition for PS-g-SPEO cast from chloroform as a function of copolymer composition

As mentioned above, the critical surface tension of both PS and stearyl is smaller than that of PEO. Therefore, it is expected that either PS or stearyl will tend to compete with each other to migrate towards and accumulate at the copolymer/air interface. However, the surface free energy of stearyl is even smaller than of PS. Furthermore, PS chains are in their glassy state and show low mobility at room temperature. These two factors make the migration and the accumulation of stearyl at the interface have a much greater probability as compared with that of PS. As we have pointed out, the motion of stearyl can force the flexible and mobile PEO chains to move with it in the same direction, therefore the final result is that SPEO migrates as a whole towards the interface and is enriched at the interface. These results demonstrate that the surface accumulation (enrichment) phenomenon of copolymer is controlled simultaneously by both the surface energy difference of the component chains and mutual restriction effect between the motion of the component chains. Or it can simply be expressed that there are two primary factors, namely surface energetics and molecular mobility, which will govern the behavior of all these systems with regard to surface/bulk differences.

Teraya^[22] has studied the surface composition of a PS-PMPEGM diblock copolymer which has the structure shown in Fig. 3a:



(a): PS/PMPEGM diblock copolymer



(b): PS-g-SPEO graft copolymer

Fig. 3 Scheme showing the molecular structures of both PS-PMPEGM diblock copolymer(a) and PS-g-SPEO graft copolymer(b)

In fact, this diblock copolymer can be regarded as a "block type" PS-g-SPEO graft copolymer with a methyl group at the free end of PMPEG (i. e. , PEO) grafting chains. And this diblock has some similarity with PS-g-SPEO excepting that the latter is a random graft copolymer (Fig. 3b). It was discovered that the PS component accumulated at the interface only when the value of n was above 9. When the value of n was not larger than 9, PMPEG (i. e. , PEO) was enriched at the interface, which was similar to the results that SPEO was enriched at the PS-g-SPEO/air interface. The reason that PMPEG could be enriched at the interface was presumed by Teraya to be caused by the hydrophobic end group effect, which meant that the surface free energy of PMPEGM was reduced because of the existence of the hydrophobic methyl end group when the chain length of PEG was very short. This example demonstrated quantitatively that PMPEG (i. e. , PEO) will accumulate at the copolymer/air interface when the ratio of the carbon atom numbers of the hydrophobic end group to the repeated unit number of EO is larger than $1/9$. As far as SPEO is concerned, this ratio equals to $18/13$ which is much larger than $1/9$. Therefore, the nature that SPEO was enriched at the interface can at least be partially attributed to the hydrophobic end group effect of stearyl.

As we have already pointed out, the effect of a kinetic factor, i. e. , the

“restriction effect” of stearyl imposing on PEO also plays an important role in causing the enrichment of SPEO at the interface. Thus, it is reasonable to conclude that the SPEO component of PS-g-SPEO is constantly enriched at the copolymer/air interface because of the synergetic function of both the hydrophobic end group effect of stearyl and the mutual restriction effect between the motion of stearyl and that of PEO.

B: Effects of bulk composition on the surface chemical composition of PS-g-SPEO.

As also shown in Fig. 2, the degree of the observed enrichment, i. e., the difference between the surface and bulk composition, varies as the bulk composition changes. For the PS-g-SPEO samples with SPEO wt% of larger than 60%, the surface with a depth of at least 5nm is fully occupied by SPEO. However, the degree of enrichment decreases a little as the bulk content of SPEO reduces when the bulk SPEO wt% of the copolymer is less than 60%.

C: Effects of casting solvents on the surface chemical composition of PS-g-SPEO.

Finally, the effect of casting solvents on the surface chemistry of PS-g-SPEO was also examined. Copolymer films were cast from ethylbenzene, a preferential solvent for PS, nitromethane, a preferential solvent for SPEO, and chloroform, a mutual solvent for PS and SPEO. As shown in Table 2, little effect was observed when the bulk SPEO content of PS-g-SPEO is rather high (Table 2, sample 11-12-5), which may be due to that the surface of PS-g-SPEO with high bulk SPEO content is fully occupied by SPEO. However, the PS content at the copolymer surface for PS-g-SPEO with lower bulk SPEO content increases as the solvent becomes more preferential for PS (sample 10-26-1 and 10-26-3 in Table 2). The latter result is similar to the case of PS-g-PEO^[21] and indicates that the evaporation of the preferential solvent of some component during the cast process will result in a surface concentration increasement of this component, i. e., the evaporation of ethylbenzene will promote the migration of PS chains to the interface, while the evaporation of nitromethane will promote the migration of PEO chains to the interface. The phenomenon that the evaporation of the preferential solvent of some component during the cast process will promote the migration of this component to the surface can be referred to as “dragging effect” of the casting solvents.

Table 2 The effect of casting solvents on the surface chemical composition of PS-*g*-SPEO graft copolymers

Sample No.	11-12-5			10-26-1 ^a		10-26-3 ^a	
Solvents	EB ^b	CHCl ₃	NM ^c	EB	CHCl ₃	EB	CHCl ₃
Bulk SPEO wt%		72.6			50.6		24.7
Surface SPEO wt%	98.5	100	99.2	70.3	84.1	39.5	46.5

a: Data for films casting from nitromethane was not presented here because PS-*g*-SPEO samples with low SPEO content can not dissolve in nitromethane

b: EB represents ethylbenzene

c: NM represents nitromethane

2. Surface wettability of PS-*g*-SPEO

As shown in the curve a of Fig. 4, the static contact angles of water on the surface of PS-*g*-SPEO graft copolymer increases nonlinearly as the PS content of the copolymer increases, indicating that the surface water wettability decreases systematically as the PS content increases, ranging from being highly hydrophilic to being fairly hydrophobic. This result also demonstrates that the surface water wettability of PS-*g*-SPEO can be controlled and adjusted in a rather wide range just by changing the composition of the graft copolymer.

As shown in the curves b and c of Fig. 4, differences in the advancing and receding contact angles are also observed ($\theta_a - \theta_r > 0$), which indicates the existence of contact angle hysteresis arising from a certain degree of surface heterogeneity. The surface heterogeneity of PS-*g*-SPEO may be related with the microphase separation morphology which will be discussed in the following text.

The static contact angle also shows a time-dependence, as illustrated in Fig. 5. θ_s decreases in a linear way as the time is prolonged, reflecting a certain degree of surface deformability. It is supposed that the water penetrates into the surface of the coatings during contact angle measurements. Then the free volume of polymer chains increases, which allows relaxation and restructuring of the surface, in such a way that the interfacial free energy of surfaces in contact with water is reduced. Therefore, hydrophilic SPEO chains thermodynamically favor water over air interface and if allowed to relax, will be exposed preferentially to water when immersed in this medium. Thus the surface content of SPEO is

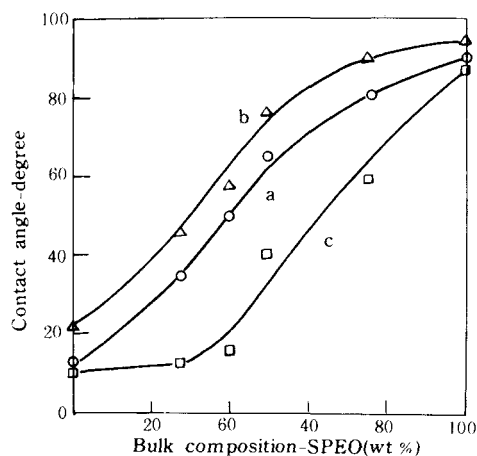


Fig. 4 Contact angles vs. bulk composition for PS-g-SPEO cast from chloroform. Curves a, b and c represent the static, advancing and receding contact angle, respectively

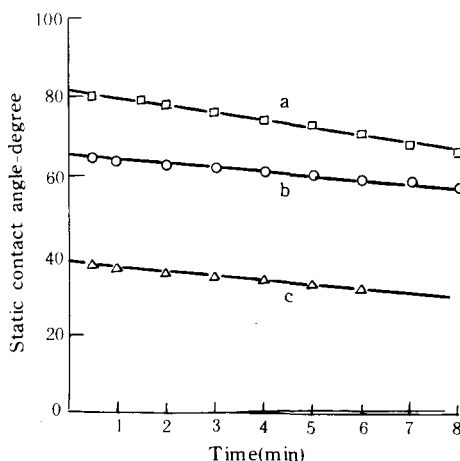


Fig. 5 Static contact angles vs. water residence time on the surface of PS-g-SPEO films. PSwt% for the samples corresponding to curves a, b and c is 75%, 49% and 27.4%, respectively

expected to increase as the time of surfaces in contact with water is prolonged, and correspondingly the contact angle decreases.

Besides, the time-dependence phenomenon of contact angle also indicates that the static contact angles on different sample surfaces should be measured in a short and fixed time to ensure that the obtained data are comparable. The data shown in the curve a of Fig. 4 were recorded at the very moment when the time of the surfaces in contact with water was 30 seconds.

3. Microphase separation morphology of PS- g -SPEO by TEM

PS-g-SPEO graft copolymers can undergo microphase separation and domain formation as clearly illustrated by TEM photographs (Fig. 6). The dark areas of the photographs correspond to PS microdomains, for PS chains are selectively stained by $\text{OsO}_4^{[17]}$. Microstructures with different shape, size and arrangement are observed by varying the chemical composition of PS-g-SPEO. An "island-sea" morphology with the "islands" of PS microdomains scattering in the "sea" of SPEO microdomains is observed when PS wt% of the copolymer is about 27% (Fig. 6a), while the shape and size of PS microdomains are similar to that of SPEO microdomains and these

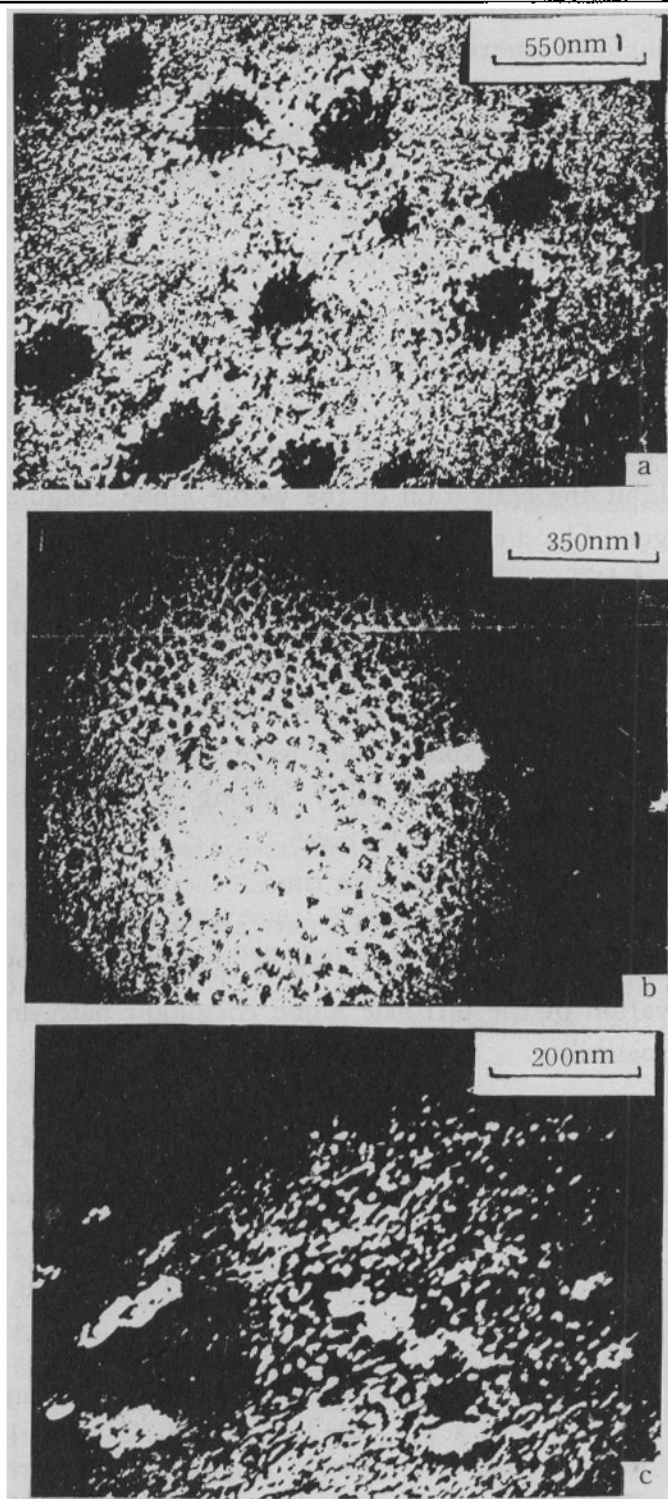


Fig. 6 Transmission electron micrographs of PS-g-SPEO copolymers. PSwt% of samples a, b and c is 27%, 53% and 75%, respectively

two microdomains disperse reciprocally and homogeneously when PSwt% is around 53% (Fig. 6b). And an "inverse island-sea" structure (Fig. 6c) is observed when PSwt% is about 75%. The meaning of "inverse island-sea" here is that PS microdomain is the "sea" and SPEO microdomain is the "island", instead of in the case of "island-sea" that "island" of PS microdomains scatter in the "sea" of SPEO microdomains.

4. *In vitro* blood compatibility assessment of PS-g-SPEO

(1) Plasma recalcification time

From Table 3, it appears that significantly prolonged RT is obtained when glass tubes coated with PS-g-SPEO are used, which indicates that PS-g-SPEO can inhibit the activation of the whole blood coagulation path and hence exhibits good blood compatibility.

The value of RT has an intimate relationship with the composition of PS-g-SPEO. Instead of showing a linear way of increment or decrement of RT as the surface SPEO content changes, a maximum value of RT is observed when the surface SPEO content is about 35%, indicating that PS-g-SPEO copolymer with suitable surface water wettability and microdomain exhibits the best blood compatibility among a series of PS-g-SPEO copolymers with different surface features.

(2) Plasma partial thromboplastin time

As also shown in Table 3, the PTTs are also significantly prolonged, as compared with that of control tubes, which indicates that PS-g-SPEO can hinder the activation of the intrinsic blood coagulant path and thus shows good-blood compatibility.

Table 3 RT and PTT of plasma on the surfaces of glass, PS, PEO and PS-g-SPEO

Sample	Bulk PSwt%	Surface SPEOwt%	RT(sec)	NRT*	PTT(sec)	NPTT*
Glass	/	/	139+7	1.0	75+3	1.0
PS	100	/	142+6	1.02	80+6	1.06
PEO	/	100	170+9	1.22	82+4	1.09
PS-g-SPEO	27.4	100	170+17	1.22	95+5	1.27
PS-g-SPEO	39.8	99	176+14	1.27	106+12	1.41
PS-g-SPEO	49.4	15.9	182+15	1.31	123+1	1.64
PS-g-SPEO	69.0	35.2	204+15	1.47	122+9	1.63
PS-g-SPEO	75.3	53.5	183+3	1.32	115+5	1.53

* Normalized data by taking glass as reference

Similar results can also be derived by analysing PTT data in Table 3, i. e. , among PS-g-SPEO samples with different surface properties, PS-g-SPEO copolymer with suitable surface water wettability and microdomain exhibits the best blood compatibility.

Keywords:

Polystyrene-g- ω -stearyl-poly(ethylene oxide); Surface properties; Graft copolymer; Blood compatible material

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